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(54) COMPOSITE PHOTO-SENSITIVE ELEMENTS

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to composite, photosensitive elements.

In both the graphic arts and electronics industry, it has become common practice to use photosensitive elements because of their high uniformity, ease of preparation, lower cost and other well-known factors. During the process of manufacture, copies must often be made which require the use of so-called "masks". These masks are copied from original "artwork" carefully prepared by draftsmen. One system, for example, prepares a copy of the artwork original on a silver halide lithographic film. This system is commonly used during the preparation of printed circuits. The silver halide film must then be "bleached" to reduce the image density so that the operator may see through the image to line up the copy while working in safelights. The safelight used here is that which masks out the ultraviolet portion of the spectrum toward which a photopolymer resist composition is sensitive; the safelight is usually a yellow color. Under this light, the black, developed silver prevents the operator from seeing through the image to line up the copy. The bleaching process, however, produces a brown color through which the operator may readily see while preparing subsequent copies. This visibility is very important as often the operator must place several image copies, one on top of the other, and the resultant "registry" must be perfect in preparing the subsequent copy. The inherent drawbacks of this system are obvious. There are numerous steps in producing the mask, such as exposure, development, bleaching, washing, all done with silver halide safelights, which, because of the inherent nature of the photographic silver halide system, are different from the photopolymer safelight system. In addition, a defect known as "pin-holes" is common to the silver halide system and subsequent passage of ultraviolet light through these pinholes produces unwanted exposure in the photopolymer copy. This defect is extremely undesirable in the printed circuit industry and cannot be tolerated. Hence, many masks must sometimes be made in order to produce one which is satisfactory, resulting in great waste and cost. In addition, the bleaching process removes excess silver which is either lost or which must be recovered from the processing solution which adds cost to the system. Finally, after several exposures, the bleached image reverts back to a highly blackened state, preventing the operator from obtaining registry, and the mask must be discarded. Thus, the life of this type mask is shortened by use.

Yet another system uses so-called "photomasks" for the preparation, for example, of integrated circuits by photolithographic techniques. These masks are copied by the process of photoreduction from the original artwork, as taught by Madlen et al. in "Integrated Circuit Engineering—Basic Technology", Chapter 3, 4th Edition (1966), published by The Boston Technical Publishers, Inc. The original artwork, termed a "photo master", is prepared 200—1000 times the actual size desired and is zealously protected because of the high cost of preparation. Photomask copies of this original are usually made on, for example, optically clear photographic glass plates coated with a fine grain, high resolution silver halide emulsion, such as the "Lippman" type. Because of the delicate and fragile nature of these masks, only a limited number of copies can be made. In addition, they, too, suffer from pin-hole defects described above. Another type of mask commonly used for this

process is taught by George and Seaman in "Photo Methods for Industry", October, 1967, pp. 66—67. These are the "metal-on-glass" type which are usually thin depositions of a Ni-Cr-Fe alloy or chromium on a glass substrate. A photoresist layer is then coated on top and the original "photo master" imaged on this photoresist by known techniques well described in the above reference. The area of the photopolymerisable layer which is left unhardened is washed off by solvent development and the metal "etched" through to the glass in these areas with special etching solutions such as inorganic acids. The remainder of the hardened photoresist is then removed and the metal image cleaned thoroughly leaving a suitable photomask. The metal mask is far superior to the emulsion mask due to its durability and ability to reproduce the original with greater fidelity. However, its manufacturing cost is very high and the number of steps required to prepare the mask make its use prohibitive in those areas where cost is a major factor. These metal masks also suffer from pinhole defects and are also relatively opaque to visible light which makes it difficult to obtain good registry.

The present invention provides a composite, photosensitive element which overcomes the disadvantages of the prior art and comprises:

(a) a photosensitive layer comprising either (i) a photohardenable material which hardens upon exposure to actinic radiation or (ii) a crosslinkable photosensitive composition which undergoes decomposition upon exposure to actinic radiation to leave material in the unexposed areas which cross-links and hardens upon treatment with a basic crosslinking agent; and, in intimate surface contact therewith,

(b) a layer of a solvent-soluble (as hereinafter defined), macromolecular organic polymer, which layer (b) contains at least one dye or pigment and is essentially opaque to ultraviolet radiation and essentially transparent to visible actinic radiation.

The layer (a) may thus contain either (i) a photohardenable material or (ii) a crosslinkable photosensitive material. Example XI illustrates the use of the latter type of material; in this Example there is used a photosensitive diazonium compound which decomposes upon exposure to actinic radiation but which cross-links in the unexposed areas when treated with ammonia to provide a solvent-insoluble material. By the term "solvent soluble" is meant that the polymer of layer (b) should be soluble in a solvent used to develop an element which has been exposed imagewise by dissolving and removing unhardened material in the unexposed or exposed areas of layer (a) while not dissolving hardened material in the remaining areas of layer (a).

Preferably the composite, photosensitive elements comprise a cover sheet (A) adherent to layer (a) and a support film (B) adherent to layer (b).

The composite film should be essentially transparent to actinic light in the visible region of the spectrum, but should, by reason of the ultraviolet dye or pigment mixed in the UV-absorbing layer (b), provide an optical density of at least 0.5 or more, e.g. up to 5.0, to that region of the spectrum to which the layer (a) is photosensitive, namely, between 200—500 mμ. The photoresist-forming layer (a) and the UV-absorbing layer (b) should adhere strongly enough to each other to resist rupture when the cover sheet (A) or support film (B) is stripped from the contiguous surface.

A mask suitable for transparent lithographic work can be provided if support film B adheres more strongly to the UV-absorbing layer (b) than cover sheet A adheres to the photoresist-forming layer (a). One exposes the photoresist-forming layer through cover sheet A, then peels off "A" for wash-off development to leave a suitable mask on support film B.

A suitable photomask can be provided by a reverse adherence factor, that is, support film B adhering less strongly to the UV-absorbing layer (b) than cover sheet A adheres to the photoresist-forming layer (a). When film "B" is peeled off, the remaining three layers can be laminated to a dimensionally stable and rigid support, for example, optical glass. After lamination and exposure, cover sheet A is removed and solvent development of layer (a) yields the photomask under the resist.

Both elements provide masks possessing all the fidelity and sharpness of currently available systems, yet masks may be produced at substantially lower cost and with considerably less handling by operators. In addition, the elements described herein are transparent to visible light allowing the operator to obtain good registry when reproducing copies from these masks. The relative low cost due to less handling permits more latitude when accidental errors or mistakes occur. Masks can be provided that are relatively free of pin-holes and other coating defects associated with silver halide emulsions or metal masks. They are also more resistant to scratches which can occur to the mask during normal handling. In addition, the masks are resistant to fading, and thus have a longer life than those silver halide systems described above. The entire system itself is compatible with other photopolymer systems allowing them to be used and handled in relatively bright safelights. This factor is important to the users of photopolymer systems such as those in the printed circuit industry. The new and useful masks can be used under the same safelight system to which they had been subjected to previously.

In a preferred embodiment the composite, photosensitive elements comprise:

(a) a photosensitive layer in intimate contact with

(b) a layer of a solvent-soluble resin, e.g. polyvinyl acetate, containing an ultraviolet radiation-absorbing agent in a concentration to provide absorption of at least 99% of actinic radiation in the region of the spectrum from 200—500 mμ, and the layer mixture, when in the form of a thin film or coating, exhibiting an optical density to the actinic radiation of 0.5 or more and preferably of 1.0 or more.

Adhesion of the two layers should be strong enough to resist rupture when the cover sheet or support film is stripped from either one of the intermediate layers. The layers may be coated or laminated together, as known to those skilled in the art. Both layers (a) and (b) preferably are disposed between the support film and cover sheet of polyethylene terephthalate or polyethylene. The support film and cover sheet serve to support or to protect both the UV-absorbing layer and the photohardenable layer.

The elements described above may be used as a transparent lithographic mask by exposing through the cover sheet, removing the cover sheet A, developing the resulting image by removing the unhardened areas of layer (a), and removing the portion of layer (b) underlying the unhardened layer (a) leaving a mask on the support film B. Concurrently, the elements described above may be used as a photomask by first stripping the support film B from the UV-absorbing layer (b), laminating the remaining three layers to a more rigid or a more dimensionally stable support C with the UV-absorbing layer (b) nearest the support, then exposing the photoresist-forming layer to actinic radiation, removing the cover sheet A on the photoresist-forming layer (a), and developing as described above, leaving a photomask on the rigid support C.

The polymeric, solvent-soluble, ultraviolet radiation absorbing layers use as binders macromolecular organic polymers that form solid films, e.g. polystyrene, copolymers of vinylidene chloride and acrylonitrile, polyacrylates and polymethacrylates, polyamides and polyvinyl esters. These polymers may have molecular weights ranging from 500—150,000 and should be soluble in solvents or developing solutions commonly used to develop photoresists, such as, for example, methyl chloroform, trichloroethylene, mixed solvents, such as methylisobutylketone-isopropanol and others known to those skilled in the art. This invention is not limited necessarily to those solvents useful for developing photoresists, however, but the solvents useful in attacking and removing the polymeric UV-absorbing layer must necessarily be unable to dissolve the hardened areas of the adjacent image. More useful elements are those in which the same solvent is used to develop the photoresist image and to simultaneously dissolve the polymer layer containing the UV-absorbing dye or pigment, resulting in less handling.

Any ultraviolet radiation-absorbing agent can be mixed with or dispersed in the solvent-soluble polymer binder or matrix, to produce the subsequent mask. Useful agents are 2,3-dihydroxybenzophenone and 2,2′-dihydroxy-4-methoxybenzophenone.

Since some photosensitive image-forming layers are also sensitive to actinic radiation just beyond the UV region of the spectrum, and since most UV dyes have rather sharp cut-off points, it is also useful to incorporate yellow or orange dyes, such as Oil Yellow 3G (Colour Index No. 29) and "Luscol" Fast Yellow T (Colour Index No. 47) with the UV-absorbing layer. Alternatively, one maye use a single dye which absorbs both in the yellow and in the ultraviolet portion of the spectrum. With respect to the UV-absorbing layer, the optical density of the ultraviolet absorber/dye/matrix layer in the actinic region should be at least 1.5—5.0 and prevent subsequent passage of actinic radiation in the spectral region which is used to initiate photosensitization, namely, from about 200—500 mμ. Photosensitive compositions and elements useful for making the layer coated over the UV absorber disclosed above, to provide a combination which will produce the dyed image to be used as the mask, are legion in number and include those uniformly crosslinkable photo hardenable materials disclosed in U.S. Patent 3,526,504, and photopolymerizable compositions of U.S. Patent 3,469,982. The photoresists crosslink when they are exposed to actinic light rich in ultraviolet radiation, as taught in U.S. Patent 3,526,504, and form a hard, polymeric surface in those exposed regions. Other useful resist or resist-like layers are described by J. Kosar in "Light-Sensitive Systems", 1965, published by John Wiley and Sons. These include the so-called "cinnamates" as described on page 140 et seq. of the above reference, dichromated colloids as described in Chapter 2 and diazo-type processes as described in Chapter 6 of the above reference as well as many other common resist formulations commercially available and well known to those skilled in the art. These layers may be coated individually on separate supports and then laminated together, or sequentially coated or extruded on top of each other and then coated or laminated on the support films or by other techniques well known to those skilled in the art. By applying so-called "subbing" layers to the support or cover sheet, one can make either the support or cover sheet

have a tendency to adhere to a stronger degree to the contiguous layer than the other.

Examples of binder or matrix compositions useful for the ultraviolet radiation-absorbing layer are as follows:

Chemical Composition	Molecular Weight	Viscosity (cps in Soln. Shown at 25°C)	Melting Point (°C)
Polystyrene Resin	1500	800 (46% toluene)	100
Polystyrene Resin	300–400	6000 (80% toluene)	75
Poly(vinylidene chloride)-acrylonitrile copolymer	–	80 (20% in methylethyl-ketone)	–
Poly (vinyl chloride)	–	40 (20% in acetone)	–
Polyamide (Melt Index of 10 at 225°C)	–	–	–15 to –10
Poly (vinyl formal)	26–34,000	–	–
Poly (vinyl butyral)	45–55,000	–	–
Cellulose acetate butyrate	–	98 (15% in benzene)	–
90 mole % methyl methacrylate 10 mole % methacrylic acid	30,000	2-ethoxy-ethanol	–
Linear γ-methyl-styrene resin	–	10,000 at 149°C. (60% in toluene)	–
Poly (vinyl chloride-vinyl acetate) copolymer (89.5–91.5 PVC)	–	–	–
Poly (vinylchloride)/maleic acid/vinyl-acetate copolymer (85–88% PVC; 0.8–1.2 MA; 10% VA)	–	70 (15% Soln. in toluene)	–
Poly (methyl methacrylate)/methacrylic acid copolymer – pH = 8	–	500 (29.5–31.5% in H_2O)	–
Chlorinated rubber* ("Parlon"–S)	–	17–25 (25% in benzene)	–
Poly (vinylpyrollidene) styrene copolymer	–	1000 (melt viscosity)	–
Poly (methyl methacrylate)	30,000	70–1400 (37.5% in toluene)	–
Poly (vinyl alcohol) 99–100% hydrolyzed		55–65 (4% in H_2O at 20°C)	–
Poly (vinylpyrrolidone)-vinyl acetate copolymer	–	25,000 (melt viscosity)	–

* 30% chlorine (Hercules Chem. Corp.)

Examples of ultraviolet dyes, ultraviolet absorbers and other dyes which can be dispersed in or mixed with the binders described above are listed below:

2,2′-dihydroxy-4-methoxy-benzophenone
4-dodecyloxy-2-hydroxybenzophenone
2,4-dihydroxybenzophenone
hydroxyphenylbenzotriazole
2(2′ - hydroxy - 5′ - methoxyphenyl)-benzotriazole
resorcinol-monobenzoate
2-hydroxy-4-methoxybenzophenone
2,2′ - dihydroxy - 4,4′ - dimethoxy - benzophenone
2,2′,4,4′-tetrahydroxybenzophenone
2 - hydroxy - 4 - methoxy - benzophenone-5-sulfonic acid
(also sodium salt of above)
ethyl-2-cyano-3,3-diphenylacrylate
2-ethylhexyl-2-cyano-3,3-diphenylacrylate

"Luxol" Fast Orange	GRL	Color	Index	#25	(Solvent Orange)
	GS	,,	,,	#24	,, ,,
	R	,,	,,	#20	,, ,,
"Plasto" Orange	M	,,	,,	#21	,, ,,
	RS	,,	,,	#22	,, ,,
Oil Orange		,,	,,	#12055	(Solvent Yellow #14)
Sudan Orange	RA	,,	,,	#12055	(Solvent Yellow #14)
Latyl Orange	3R	,,	,,	#26	(Disperse Orange)
Capracyl Orange	R	,,	,,	#60	(Acid Orange)
"Luxol" Fast Yellow	G	,,	,,	#45	(Solvent Yellow)
	T	,,	,,	#47	,, ,,
"Plasto" Yellow	GR	,,	,,	#39	,, ,,
	MGS	,,	,,	#40	,, ,,
Oil Yellow	3G	,,	,,	#29	,, ,,
	N	,,	,,	#2	,, ,,
Sudan Yellow		,,	,,	#30	,, ,,
Latyl Yellow	3G	,,	,,	#54	(Disperse Yellow)
Latyl Orange	NST	,,	,,	#25	(Disperse Orange)
Capracyl Yellow	N	,,	,,	#113	(Acid Yellow)
Latyl Yellow	YWL	,,	,,	#42	(Disperse Yellow)
Capracyl Yellow	NW	,,	,,	#113	(Acid Yellow)
Capracyl Orange	R	,,	,,	#60	(Acid Orange)
Bakcar Yellow	CY	,,	,,	#75	(Disperse Orange)
Yellow	2G	,,	,,	#3	(Disperse Yellow)
Primrose Yellow		,,	,,	#77603	(Pigment)
Chrome Yellow	Light	,,	,,	#77603	,,
Chrome Yellow	Medium	,,	,,	#77600	,,

Dispersed Manganese dioxide					
Toluidine Yellow	GW	,,	,,	#71680	,,
Molybdate Orange		,,	,,	#77605	,,
Dalamar Yellow		,,	,,	#11741	,,
Green Gold		,,	,,	#12775	,,
Graphtol Yellow		,,	,,	Pigment Yellow #61	
Graphtol Orange		,,	,,	Pigment Orange #13	
Victoria Pure Blue	BO	,,	,,	#42595	

This invention will be further illustrated by the following examples.

EXAMPLE I.

The following two solutions were prepared:

Solution A (for use in Preparing the UV Absorber Layer)

- 1600 gm 15% acrylic hydrosol in water, which is a terpolymer made from 55% methyl methacrylate, 40% ethyl acrylate and 5% acrylic acid, 30% solids by weight with a particle size of 0.01—0.05 micron.
- 95 gm Capracyl Yellow NW, Colour Index #113
- 95 gm Capracyl Orange R, Colour Index #60
- 35 gm Bakcar Yellow CY, Colour Index #75
- 50 gm Yellow 2G, Colour Index #3
- 1000 gm Water

This mixture was stirred for one hour and then the following was added:

- 20 gm trimethylolpropane triacrylate
- 5 gm concentrated sodium lauryl sulfate (10% in water)
- 10 gm 10% water solution of a fluorinated hydrocarbon which possesses the following chemical structure:

$$(C_8F_{17}-SO_2-\underset{\displaystyle |}{\overset{CH_2-CH_3}{N}}-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus})K^{\oplus}$$

Solution B (for use in Preparing the Photoresist Layer)

- 600 gm copolymer of methylmethacrylate (90 mole %) and methacrylic acid (10 mole %)
- 24 gm dimer of o-chlorophenyl-4,5-bis(m-methoxyphenyl)imidazole
- 12 gm 4,4' - bis(dimethylamino)benzophenone
- 72 gm mixed ester of triethyleneglycol-dicaproate and -dicaprylate
- 300 gm trimethylolpropanetriacrylate
- 200 gm 2-(2-ethoxy)ethanol
- 4292 gm trichloroethylene

Viscosity=16 cps. at 25°C using a #1 spindle in the Brookfield Viscometer

Solution A was machine coated on 0.18 mm thick polyethylene terephthalate clear film prepared as described in Example IV of U.S. Patent 2,779,684, containing a resin sub layer on one side only. Solution A was coated on the resin subbed side using an air knife as known to those skilled in the art. After heating and drying Solution B was coated on top of A in the same manner and the resulting product laminated with a 0.019 mm thick, clear, biaxially oriented and heat-set polyethylene terephthalate film to yield a composite element having the structure set forth above, where A is biaxially-oriented and heat-set polyethylene terephthalate, (a) is a photopolymerizable layer (from Solution B) about 0.0025 mm in dry thickness, (b) is the UV-absorbing layer (from solution A), approximately 0.0025 mm dried thickness and B is resin subbed polyethylene terephthalate film. The finished product was given a 2-minute exposure to a carbon arc ("nuArc" xenon lamp, "Flip-Top" Plate Maker Model FT26M—2) at a distance of 45.7 cm through a test image which was a stencil drawing simulating a printed circuit. After stripping off sheet A, the photoresist image formed on (a) was developed in the following solution:

- 60 ml 2-(2-Butoxy)ethanol
- 2 ml octylphenoxyethoxy ethanol
- 66.5 gms sodium silicate solution (60% solids in water)
- Water to 1 liter

This solution not only developed the photoresist image on the photopolymer but also dissolved the polymeric UV-absorbing layer in the identical area under the image producing a yellow colored, exact positive copy of the original which was useful for preparing other copies.

EXAMPLE II.

The following two solutions were prepared:

Solution A

1000 gm	poly(vinyl acetate)—having a viscosity of 13 to 18 cps as an 8.6% solution in benzene at 20°C.
60 gm	terpolymer made by reacting 1200 gm methyl methacrylate, 50 gm methacrylonitrile and 500 gm methacryloxypropyltrimethoxysilane which had a molecular weight of 15,700 and an analysis of 1.03% N and 3.15% silicon
100 gm	trimethylolpropane trimethacrylate
100 gm	2,2′ - dihydroxy - 4 - methoxybenzophenone
100 gm	"Luxol" Fast Yellow—T, Colour Index #47
100 gm	ethyl alcohol
14500 gm	trichloroethylene

This solution contained about 7% solids and had a viscosity of 17 cps at 25°C.

Solution B

578 gm	poly(methyl methacrylate) — molecular weight 30,000
220 gm	poly(methyl methacrylate) — molecular weight 60,000
95 gm	terpolymer described in "A"
835 gm	trimethylolpropane trimethacrylate
135 gm	triethyleneglycol diacetate
24 gm	o - chlorophenyl - 4,5 - bis(n-methoxyphenyl)-imidazole dimer
9 gm	7 - diethylamino - 4 - methylcoumarin
9 gm	2-mercaptobenzothiazole
1,000 gm	methyl alcohol
7975 gm	methylene chloride

This solution contained about 17.5% solids. Solution "A" was coated on 0.023 mm-thick clear, biaxially oriented and heat set polyethylene terephthalate film. Coating was accomplished by the use of a "doctor" knife. After drying, the film was laminated with 0.025 mm-thick polyethylene to protect the resulting UV-absorbing layer which had a dried thickness of about 0.010 mm and the following optical densities, as observed on a Cary Optical Spectrophotometer:

450 mμ=1.73
400 mμ=2.59
350 mμ=3.32
300 mμ=2.25

This UV-absorbing layer was next transferred to a 7.62 cm × 10.16 cm projector slide cover glass, which had been thoroughly cleaned by scrubbing with solvents. Transfer was accomplished by removing the polyethylene cover sheet and laminating the UV-absorbing layer to the glass plate through heated rollers at 100—120°C at approximately 1.83 m/min.

Solution B was coated on 0.019 mm-thick, clear biaxially oriented and heat set polyethylene terephthalate base in the same manner. After drying, this photoresist layer, which was about 0.010 mm-thick, was laminated with a polypropylene cover sheet to protect the imaging layer during subsequent handling.

The polyethylene terephthalate support film was stripped from the UV-absorbing layer which had been firmly laminated to the glass and the polypropylene cover sheet removed from the photoresist layer and the two layers laminated together as described above, providing a laminated photopolymerizable element having the structure set forth above, where A is polyethylene terephthalate, (a) is photopolymerizable layer, (b) is UV-absorbing layer, and B is glass.

The photopolymerizable layer (a) was then given a 10-second exposure at 40.6 cm with a 1000-watt quartz iodide lamp through a negative containing a standard test pattern comprised of simulated electronic printed circuitry. The polyethylene terephthalate sheet A was removed by stripping and the resulting image developed by dipping in a solution consisting of 90% methylisobutylketone/10% isopropanol, followed by a water spray, and the resulting yellow image dried by blowing with compressed air. The solvent used herein dissolved both the unhardened areas of the photoresist and subsequently the dyed, polymeric underlayer leaving a suitable, positive mask on a rigid glass support useful for imaging photoresists with light sensitivity of between 300—450 mμ.

EXAMPLE III.

The same compositions outlined in Example II were prepared and coated on their respective substrates as previously described. After stripping off the protective polyethylene cover sheet from the UV-absorbing layer Solution A, it was laminated by the same technique to a piece of clear poly(methylmethacrylate). The photoresist layer was next joined to the UV-absorbing layer on the poly(methylmethacrylate), as previously described, to form a composite film element having the structure that is set forth above, where A is polyethylene terephthalate, (a) is photoresist, (b) is UV-absorbing layer and B is poly(methylmethacrylate). A negative test image was exposed through layer A on to layer (a) with a six-second exposure to a 1000-watt quartz-iodide lamp at a distance of 40.64 cm. Layer A was removed and the photoresist image developed by spraying with methylchloroform for 30 seconds followed by a second spray of 2-methoxyethanol and a prolonged water spray. The positive yellow image on the rigid poly(methylmethacrylate) support suitable for use as a photomask, was then dried with compressed air.

EXAMPLE IV.

Solution A, for use as the UV-absorbing layer, was prepared as follows:

2000	gm	of the acrylic hydrosol described in Example I
50	gm	10% sodium lauryl sulfate in water
30	gm	fluoronated hydrocarbon, 10% water solution as described in Example I

This slurry was heated to 35°C and the mixture shown below was added slowly:

40	gm	Latyl Yellow 3G, Colour Index #54
35	gm	"Luxol" Fast Orange GS, Colour Index #24
20	gm	2,2' - dihydroxy - 4 - methoxybenzophenone

This material was coated on 0.18 mm-thick polyethylene terephthalate clear film subbed, and prepared as described in Example IV of U.S. Patent 2,779,684, using a "doctor" knife resulting in a dried coating which was 0.005 mm thick. Once again, this coating was laminated with a thin sheet of polyethylene to prevent damage to the surface during storage and transfer. After removal of this cover sheet, the photoresist element of Example II was laminated to the UV-absorbing layer on the resin-subbed polyester to form a laminated photopolymerizable element having the composite structure that is set forth above, where A is polyethylene terephthalate, (a) is photoresist (b) is UV-absorbing layer and B is resin-subbed polyethylene terephthalate. A negative test image was laid on top of A, exposed 10 seconds to a 1000-watt quartz iodide lamp at a distance of 40.64 cm. A was stripped off and the photoresist image on (a) developed by spraying for 35 seconds with methyl chloroform followed by a 15-second spray with 2-(2-butoxy) ethanol and a 1-minute spray with water. This development procedure also dissolved the UV-absorbing layer in the same area below the image. The resulting orange-yellow image was dried with compressed air to provide a photomask. A photopolymerizable material of the following composition was then prepared:

525	gm	poly(methyl methacrylate), mol. wt. 30,000
300	gm	poly(methyl methacrylate), mol. wt. 60,000
525	gm	trimethylolpropane triacrylate
128	gm	triethyleneglycol diacetate
9	gm	4,4' - bis(diethylamino) benzophenone
42.3	gm	o - chlorophenyl - 4,5 - bis(n-methoxyphenyl)-imidazole dimer
2.1	gm	tri(4 - diethylamino - 3-methyl)phenyl methane
500	gm	methyl alcohol
7970	gm	methylene chloride

Viscosity=17 cps at 25°C

This material was coated on 0.019 mm clear, biaxially oriented and heat-set polyethylene terephthalate film yielding a dried thickness of 0.008 mm and laminated with a cover sheet of polypropylene. The photopolymerizable layer had a light sensitivity extending from 300—400 mμ. After removal of the polypropylene cover sheet, this photoresist was laminated to a sheet of anodized aluminum by the hot roller technique described in Example II. The photomask prepared above was then laid on top of the polyethylene terephthalate cover film and exposed 5 seconds at 40.64 cm using the 1000-watt quartz iodide source. After stripping the polyethylene terephthalate film off, the photoresist image was developed by spraying with methyl chloroform for 30 seconds and water for 1 minute. The anodized aluminum was etched in those areas where the photoresist layer had been removed by dipping in a 10% aqueous sodium hydroxide solution leaving an exact replica of the photomask firmly etched on the aluminum plate.

EXAMPLE V.

Solution A, for use as the UV-absorbing layer, was prepared as follows:

100	gm	5% poly(vinylacetate) in water (viscosity is 55—65 cps at 20°C using the Hoeppler falling ball method)
1	gm	Oil Yellow 3G, Colour Index #29
1	gm	"Luxol" Fast Yellow T, Colour Index #47
1	gm	2,2' - dihydroxy - 4 - methoxybenzophenone
50	ml	ethyl alcohol

After vigorous stirring this mixture was coated on polyethylene terephthalate clear film prepared and subbed in the manner as described in U.S. Patent 3,443,950 and which has been also coated with a thin anchoring substratum of gelatin (0.5 mg/dm^2). After drying, the UV-absorbing layer had a thickness of 0.05 mm. The photoresist element of Example II comprising the photopolymerizable layer (a) and polyethylene terephthalate base A was laminated on top of the dried UV-absorbing layer to form a composite photopolymerizable film having the structure that is set forth above, where A is polyethylene terephthalate, (a) is photoresist, (b) is UV absorber layer and B is gel-subbed polyethylene terephthalate. A test image was laid on A and exposed 30 seconds to a "nuArc" xenon arc lamp at a distance of 40.64 cm. Layer A was then stripped off and the photoresist image developed by spraying for 25 seconds with methyl chloroform followed by 25 seconds

of hot water spray and 15 seconds of cold water spray. The resultant image, with a dyed underlayer replicate, made an excellent photomask.

EXAMPLE VI.

Solution A, for use as the UV-absorbing layer, was prepared as follows:

2000	gm	15% acrylic hydrosol (described in Example I)
35	gm	Dalamar Yellow, Colour Index #11741
0.5	gm	sodium laurylsulfate
0.05	gm	Victoria Pure Blue BO, Colour index #42595
1.5	gm	2,2' - dihydroxy - 4 - methoxybenzophenone
5	gm	trimethylolpropane triacrylate

This solution was stirred for two hours and coated on 0.18 mm polyethylene terephthalate resin-subbed base described in Example III to a dry thickness of 0.05 mm. This material had an optical density of 5—7 between 300 and 500 mμ. A photoresist slurry was then prepared which had the following composition:

5	gm	poly(methyl methacrylate) mol. wt. 30,000
1	gm	triethyleneglycol diacetate
3	gm	trimethylolpropane triacrylate
0.1	gm	benzophenone
0.1	gm	4,4' - bis(dimethylamino)benzophenone
1	gm	ethyl alcohol
		methylenechloride to 50 gm.

This solution was coated on 0.019 mm-thick polyethylene terephthalate and then laminated to the UV-absorbing layer, as previously described, yielding a composite photopolymerizable film having the structure that is set forth above, where A is polyethylene terephthalate, (a) is the photoresist, (b) is the UV-absorbing layer, and B is resin-subbed polyethylene terephthalate. This sandwich was exposed 5 seconds to a SG—60 "Sun Gun" (1000-watt) at a 40.64 cm distance through a photographic, silver halide negative test image laid on top of layer A. Layer A was stripped off and the photoresist image developed by spraying for 10 seconds with chloroform. A 25-second spray with 2-ethoxyethanol followed by a 1 minute water wash completed the development and removed that area of the UV layer under the unexposed region of the photoresist that had already been dissolved. After drying, the green colored positive photomask obtained was used to expose the following light-sensitive materials:

1. A photopolymer printing plate described in U.S. Patent 3,458,311 was exposed through this mask for 45 sec. at 91.44 cm under the stand-up carbon arc. The line and halftone pattern was developed with the developer composition disclosed in the above reference and a suitable printing plate was obtained.
2. The following "tacky" photopolymer system was prepared:

40.2%	poly(methyl methacrylate), mol. wt. 30,000
50.2%	polyoxyethylated trimethylolpropane triacrylate
5.6%	poly(oxyethylene)lauryl ether
0.16%	2-mercaptobenzothiazole
0.16%	7 - diethylamino - 4 - methylcoumarin
1.6%	o - chlorophenyl - 4,5 - bis(m-methoxyphenyl) - imidazole dimer
25%	solids in trichloroethylene

   This material was coated to a dry thickness of 0.010 mm on resin subbed polyethylene terephthalate and overcoated by laminating a 0.019 mm-thick polyethylene terephthalate sheet on top. The photomask was imaged on this material by exposure to the xenon arc for 15 seconds at 45.7 cm. The image, which is formed by the hardening of the tacky polymer in the area which was exposed, was developed after removal of the polyethylene terephthalate cover sheet by dusting with a dry, colored dye which adhered to those tacky portions. This material is described in U.S. Patent 3,307,943. The resultant dyed image was transferred to coated paper stock by lamination at 110°C and an excellent positive copy of the photomask was thus secured.
3. A moderately slow, ortho-sensitive silver halide film (mainly chlorobromide with small amounts of iodide) was exposed for 10 seconds to the same photomask using a General Electric 100-watt, 20-volt standard incandescent lamp at a distance of 134.6 cm, through a 0.6 neutral density filter and a #47 Wratten filter. The image was developed in a standard multiprocess type developer (metol-hydroquinone) followed by fixing in a conventional photographic fixer, washed and dried as known to those skilled in the art. A very high resolution black and white image was obtained.

EXAMPLE VII.

A slurry for use as the UV-absorbing layer was prepared by placing the following components in a ballmill mixer:

500	gm	15% acrylic hydrosol (same as material described in Example I)
50	gm	10% aqueous saponin solution
30	gm	Latyl Yellow YWL, Colour Index #42
8	gm	Latyl Orange NST, Colour Index #25

10 gm	trimethylolpropane triacrylate
25 gm	"Cymel" (urea-formaldehyde copolymer produced by American Cyanamid Co.)
5 gm	2,2' - dihydroxy - 4 - methoxybenzophenone

After mixing for 16 hours, the slurry was filtered through felt and coated to a dried thickness of 0.05 mm on polyethylene terephthalate resin subbed as described in Example IV. The film was then heated to coalesce the polymer upon which a transparent, orange colored film was obtained which exhibited the following optical densities as measured on a Cary Spectrophotometer:

Wavelength (mμ)	Optical Density
500	>4.52
400	>4.52
350	>2
300	>2

The photoresist element described in Example II was then laminated to this layer in the same manner and exposure-development carried out as described in that Example. This mask material was useful for imaging photoresist clad copper circuit boards.

EXAMPLE VIII.

The following two solutions were prepared:

Solution A (for use in preparing the ultraviolet absorbing layer)
The same as described in Example I.

Solution B (for use in preparing the photoresist layer)

Poly(methyl methacrylate/methacrylic acid) — 90/10 mole ratio	53.8 per cent
Pentaerythritol triacrylate containing 0.4% of p-methoxyphenol as thermal inhibitor	44.1 per cent
Tertiary-butylanthraquinone	2.0 per cent
Ethyl Violet (CI Basic Violet 4) Dye	0.1 per cent

The above are represented as percentages of a solution (containing 20% solids) in methyl ethyl ketone/isopropanol 3/1.

Solution A was coated on 0.18 mm-thick polyethylene terephthalate as described in Example I and dried. Solution B was then coated on top of A to a coating weight of approximately 87 mg/dm² solids and dried. This composition was then overcoated with a 3% aqueous solution of polyvinyl alcohol (medium viscosity, 99% saponified) containing 2% of a polyoxyethylene surfactant as disclosed in U.S. Patent 3,458,311, Example I. The resulting, dried polyvinyl alcohol coating weight was 12 mg/dm. The composite coating was then given a 30-second exposure to a "nuArc" "Flip-Top" Plate Maker, Model FT 26M—2 stand-up carbon arc through a test image simulating an integrated electrical circuit at a distance of 43.18 cm and the resulting photoresist image developed using a developer of the following composition:

Isopropyl alcohol (99%)	10%	by volume
Sodium hydroxide	0.1%	by weight
Water	89.9%	by volume

The plate was covered by the developer and allowed to soak for 30 seconds. The entire protective layer, along with the unexposed areas of the photopolymerizable layer and the dyed polymer layer underneath the corresponding areas was removed by sponging. The developed plate was rinsed in water and dried and a yellow colored copy of the original was produced which was suitable for use as a mask.

It is not essential to provide the element layers interposed between a support and cover sheet. Other modifications can be made, for example, by providing the UV-absorbing layer (b) with sufficient thickness so that a portion of that layer can be thermally hardened to provide support for the element. Moreover, removal of the cover sheet can provide a practical system. The modifications described and shown are preferred.

EXAMPLE IX.

Solution A (the UV absorber layer) was prepared and coated on 0.18 mm-thick polyethylene terephthalate film as described in Example I. A cross-linkable isoprene resist which has been identified by W. L. Hunter and P. H. Crabtree and reported in Photographic Science and Engineering, Vol. 13, No. 5, p.271 (1969) (sold by Eastman Kodak Company as "Kodak Thin Film Resist") was coated on top of the dried UV absorber layer using a 0.05 mm doctor knife. After drying the resist layer at 38°C for 2 minutes, it was exposed to a test image as described in Example I and the resulting product developed in a xylene based developer furnished by the manufacturer of the resist formulation (Eastman Kodak Co. "Metal Etch Resist Developer") by soaking for 10 minutes at room temperature. The plate was then rinsed in a 50/50 mixture of ethyl alcohol and water. The resulting mask which was produced was suitable for preparing other copies.

EXAMPLE X.

Solution A of Example I (for the UV absorber layer) was prepared and coated as in Example IX and dried. The following mixture was then coated on top using a 0.05 mm doctor knife:

10 g. photographic grade gelatin
90 g. distilled water
5 g. potassium dichromate
5 g. 10% aqueous saponin solution

The gelatin was dissolved in the water by soaking at 38°C. and the potassium dichromate and saponin then added slowly with stirring. After coating this mixture on the UV absorber layer above, the coating was dried with warm air and the resulting plate given a 5 minute exposure through the test image using the same exposure conditions and light source as in Example I. The exposed film was then developed by soaking 30 seconds in the following solution:

9.6 g. sodium borate decahydrate
2.0 g. 10% octylphenoxy ethanol in water
180.0 g. 2-(2-butoxy ethanol)
Water to 1 liter

The developed image was then rinsed in cold water and dried. A yellow copy of the original, opaque to radiation between 200—500 mμ, and suitable for use as a mask of the original remained.

EXAMPLE XI.

Solution A (the UV absorber layer) was prepared and coated as described in Example IX. A crosslinkable, photosensitive composition was prepared as described in Example I of Specification No. 1,324,548 by dissolving 0.5 g of (1,4 - butanediol)dibenzoate 4,4'-bis(diazonium zinc chloride) in 25 ml of acetone containing 2.5 g. of poly(methylmethacrylate/hydroxyethyl methacrylate) ($\overline{MW}\simeq$ 30,000; 90 mole percent methylmethacrylate), 0.5 g p-toluenesulfonic acid, 1.0 g triethylene glycol diacetate, 2 cc of ethanol and 1 ml of water; the composition was coated on top of the dried UV absorber layer. A test image was then placed on the dried, photosensitive layer and exposed for 2 minutes at a distance of 61 cm to a 2,500-watt, 14 ampere carbon arc, treated with ammonia fumes and then developed by washing out the exposed areas with 1,1,1-trichloroethane. The solvent used to develop the element by washing out the exposed areas of the photosensitive composition also removed the same areas of the UV absorber layer leaving a positive image of the original which was suitable for use as a photomask for imaging subsequent copies.

EXAMPLE XII.

Solution A (the UV absorber layer) was prepared, coated and dried as in Example IX. A diallyl isophthalate prepolymer was then made according to the method of U.S. Patent 3,376,139. This photosensitive prepolymer was then dissolved in methyl isobutyl ketone (about 5:1 solvent:prepolymer) and sensitized by adding 4,4'-bis(dimethylamine)benzophenone (0.01 g. of the sensitizer per 6.5 g. solution). The resulting solution was spray coated on top of the above UV absorber layer and dried. The dried layer was about 0.003 mm thick. The test image was then laid on top of this element and exposed as in Example I and the resulting product developed by soaking for 30 seconds in 1,1,1-trichloroethane. A colored copy of the original was obtained which was suitable for preparing further copies.

EXAMPLE XIII.

The following solution was prepared:

Copolymer of ethyl acrylate (ca. 88%) and acrylic acid (ca. 12%)*	100 g.
NH_4OH solution (Saturated, approx. 58% NH_3)	12 g.
Distilled water	888 g.

50 g. of this solution was mixed with 50 g. of the acrylic hydrosol described in Example I plus 5 g. of 25% water solution of a fluorinated hydrocarbon of the structure described in Example I. Then, 10 g. of solid potassium permanganate were added and the mixture stirred for 2 hours until all gas evolution ceased. 10 ml of 2-(2-ethoxy ethanol) was added and the solution coated on 0.13 mm thick polyethylene terephthalate film as in Example I using a 0.05 mm doctor knife to yield a dry coating weight of 50 mg/dm². This structure was then overcoated with the photosensitive resist formulation of Example I (Solution B) and laminated, exposed to a test image and developed in the same manner as described in Example I. The brown, MnO_2 copy of the original image absorbed strongly between 200—500 mμ and was a useful mask-copy of the original.

[The terms "LUXOL", "PARLON", "PLASTO", "nuArc", "Flip-Top", "Sun-Gun" and "Cymel" are Registered Trade Marks.]

WHAT WE CLAIM IS:—

1. A composite, photosensitive element which comprises:

(a) a photosensitive layer comprising either (i) a photohardenable material which hardens upon exposure to actinic radiation or (ii) a crosslinkable photosensitive composition which undergoes decomposition upon exposure to actinic radiation to leave material in the unexposed areas which crosslinks and hardens upon treatment with a basic crosslinking agent;

* This copolymer is a thermoplastic acrylic polymer molecular weight approximately 260,000 and containing a number of carboxylic acid groups. The $NH_4^{\oplus}$ salt formed in the above solution has a tensile strength of 4100 PSI.

and, in intimate surface contact therewith,

(b) a layer of a solvent-soluble (as hereinbefore defined), macromolecular organic polymer which layer (b) contains at least one dye or pigment and is essentially opaque to ultra-violet radiation and essentially transparent to visible actinic radiation.

2. An element according to claim 1, wherein the layer (a) is adherent to a cover sheet and the layer (b) is adherent to a support film.

3. An element according to claim 1 or 2, wherein layer (b) has an optical density of 1.5 to 5.0 in the region of the actinic spectrum responsible for initiation of the photosensitising reaction.

4. An element according to any one of the preceding claims, wherein the layer (a) comprises, as photohardenable material, an addition polymerisable monomer and a polymeric binder.

5. An element according to claim 4, wherein the addition polymerisable monomer contains at least one methacrylate group.

6. An element according to any one of claims 1 to 3, wherein the layer (a) comprises a photohardenable material which is uniformly crosslinkable.

7. An element according to claim 2, wherein the support film has greater adherence to layer (b) than the cover sheet has to layer (a).

8. An element according to claim 2, wherein the support film has lesser adherence to layer (b) than the cover sheet has to layer (a).

9. A composite photohardenable element according to Claim 1 substantially as hereinbefore described.

10. A process for the preparation of a coloured mask which comprises imagewise exposing to actinic radiation a composite element as claimed in any one of claims 2 to 8, the element being exposed through the cover sheet adherent to layer (a), removing the cover sheet, removing the unhardened areas of layer (a) and removing the portion of layer (b) underlying the unhardened areas of layer (a).

11. A process according to claim 10 wherein the portion of layer (b) underlying the unhardened areas of layer (a) is removed by washing those portions with a solvent for the material of layer (b).

12. A process according to claim 10 wherein the unhardened areas of layer (a) are removed by washing the element in a liquid which is a solvent for both the material in the unhardened areas of layer (a) and for the material of layer (b).

13. A process for the preparation of a coloured mask which comprises removing the support film from an element as claimed in any one of claims 2 to 8, laminating the element to a rigid support, with the layer (b) nearest the rigid support, exposing the layer (a) imagewise to actinic radiation, removing the cover sheet on the layer (a) and removing the unhardened areas of the layer (a) and the portion of the layer (b) underlying the unhardened areas of layer (a) leaving a photomask on the rigid support.

14. A process for the preparation of a coloured mask from an element as claimed in any one of claims 1 to 9 substantially as hereinbefore described.

15. Coloured masks whenever prepared by a process as claimed in any one of claims 10 to 14.

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